



AFRL-SN-WP-TP-2007-107

MID-IR TRANSITION METAL LASERS (POSTPRINT)

Kenneth L. Schepler

**Electro-Optics Countermeasures Technology Branch
Electro-Optics Sensor Technology Division**

JANUARY 2007

Approved for public release; distribution unlimited.

See additional restrictions described on inside pages

STINFO COPY

**AIR FORCE RESEARCH LABORATORY
SENSORS DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7320
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE**

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YY) January 2007		2. REPORT TYPE Conference Paper Postprint		3. DATES COVERED (From - To) 01 June 2006 – 31 January 2007	
4. TITLE AND SUBTITLE MID-IR TRANSITION METAL LASERS (POSTPRINT)				5a. CONTRACT NUMBER In-house	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61102F/62204F	
6. AUTHOR(S) Kenneth L. Schepler				5d. PROJECT NUMBER 2003	
				5e. TASK NUMBER 12	
				5f. WORK UNIT NUMBER 20031224	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Electro-Optics Countermeasures Technology Branch Electro-Optics Sensor Technology Division Air Force Research Laboratory, Sensors Directorate Wright-Patterson Air Force Base, OH 45433-7320 Air Force Materiel Command United States Air Force				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-SN-WP-TP-2007-107	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Sensors Directorate Wright-Patterson Air Force Base, OH 45433-7320 Air Force Materiel Command United States Air Force				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RYPJW	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-SN-WP-TP-2007-107	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Published in Proceedings of SPIE, Vol. 6451 (2007). This is a work of the U.S. Government and is not subject to copyright protection in the United States. Report contains color.					
14. ABSTRACT Transition metal ions have been of great interest from the beginning of laser development because of their broadband emission. The first demonstration of a transition metal laser used Ni ²⁺ as the active ion in 1963. Other transition metal ions such as Co ²⁺ have also been developed as lasers but low cross sections and the need for cryogenic cooling to achieve high efficiency hindered their transition from discovery to applications. The 1995 innovation of pairing Cr ²⁺ with a host that has tetrahedral symmetry substitution sites led to demonstration of broadly tunable, room temperature, mid-IR lasers. Progress in advancing this class of transition metal laser to output power of 18 W, tuning range to several hundred nanometers, and modelocked operation down to 100 fsec will be reviewed. Plans for future development in the areas of femtosecond pulse operation, high speed frequency tuning, fiber format, and direct electronic pumping will be discussed.					
15. SUBJECT TERMS transition metal lasers, infrared, chromium, solid-state, chalcogenide					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON (Monitor) Kenneth L. Schepler 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Mid-IR transition metal lasers

Kenneth L. Schepler

Air Force Research Laboratory, Wright-Patterson AFB, OH USA 45433-7304

ABSTRACT

Transition metal ions have been of great interest from the beginning of laser development because of their broadband emission. The first demonstration of a transition metal laser used Ni^{2+} as the active ion in 1963. Other transition metal ions such as Co^{2+} have also been developed as lasers but low cross sections and the need for cryogenic cooling to achieve high efficiency hindered their transition from discovery to applications. The 1995 innovation of pairing Cr^{2+} with a host that has tetrahedral symmetry substitution sites led to demonstration of broadly tunable, room temperature, mid-IR lasers. Progress in advancing this class of transition metal laser to output power of 18 W, tuning range to several hundred nanometers, and modelocked operation down to 100 fsec will be reviewed. Plans for future development in the areas of femtosecond pulse operation, high speed frequency tuning, fiber format, and direct electronic pumping will be discussed.

Keywords: transition metal lasers, infrared, chromium, solid-state, chalcogenide

1. INTRODUCTION

Transition metal ions have been of great interest from the beginning of laser development because of their broadband emission. Basically, transition metals are broadly tunable laser active centers because the partially-filled, electronic d orbitals extend far from the nucleus and interact strongly with the surrounding lattice. The lattice interaction provides strong vibrational coupling giving rise to broad absorption and emission features. In contrast, rare earth active ions have partially filled f levels that are screened from lattice interactions by the filled d levels.

Ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$), the first demonstrated laser medium, [1] turned out to be an exception to the rule that transition metal lasers are broadly tunable. So tunable chromium ion lasing was not discovered until Cr^{3+} :alexandrite was demonstrated in 1979. [2] Cr^{4+} and Cr^{2+} infrared laser materials took even longer to be discovered. However, transition metal laser development actually had an early start with flashlamp-pumped demonstration of Ni^{2+} [3] and Co^{2+} [4] doped fluoride hosts as discussed in more detail below.

This paper will review the development of infrared lasers based upon stimulated emission from transition metal ions. A historical review will be followed by an emphasis on recent development of room temperature Cr^{2+} lasers. Current performance records will be discussed next and finally, current issues will be addressed.

2. EARLY TRANSITION METAL INFRARED LASERS

The first demonstration of an infrared transition metal laser was in 1963 and used Ni^{2+} in MgF_2 operating at 1.63 μm with flashlamp pumping and cryogenic cooling. [3] A cryogenically cooled Co^{2+} laser was demonstrated the next year with operation at various wavelengths in the 1.75-2.15 μm region. [4] Co^{2+} ($3d^7$ configuration) and Ni^{2+} ($3d^8$ configuration) have two and three unpaired electrons respectively. The free-ion levels split in an octahedral symmetry crystal field when these ions substitute for Mg^{2+} in crystals like MgF_2 . The crystal field splitting gives rise to the observed broadband absorption and emission features. But spectral laser tuning is often less than the observed fluorescence of these active ions. This restriction in tuning range was found to be caused by excited state absorption. [5] Efficient laser operation requires cryogenic cooling due to a rapid decrease in fluorescence lifetime [6, 7] with increasing temperature. This decrease in lifetime is caused by the rapid increase of nonradiative multi-phonon relaxation with increasing temperature.

Greater than 30% efficient cw operation of cryogenically cooled $\text{Co}^{2+}:\text{MgF}_2$ lasers has been demonstrated. [8, 9] But all cw operation has required cryogenic cooling. Pulsed operation of $\text{Co}^{2+}:\text{MgF}_2$ lasers at room temperature has been

demonstrated at the expense of higher threshold and lower efficiency. [10] However, if the pump pulse is maintained shorter than the lifetime of the upper laser level the efficiency and threshold can approach the cryogenic levels. Pulse energy is limited by the surface damage threshold of the host material.

Use of Ni^{2+} and Co^{2+} lasers in infrared applications has been meager. While $\text{Co}^{2+}:\text{MgF}_2$ lasers were at one time commercially available, the need for cryogenic cooling has limited their potential to one-of-a-kind laboratory uses.

3. Cr^{2+} TRANSITION METAL LASERS

The large phonon energies in oxide and fluoride host crystals lead to nonradiative relaxation rates that exceed radiative relaxation rates for many active ions at room temperature. This results in poor laser performance for infrared transition metal ions when operated at or near room temperature. The nonradiative rate depends upon the number of phonons p required to equal the energy gap ΔE as shown in Equation 1 and Figure 1.

$$p = \Delta E / h\nu \quad (2)$$

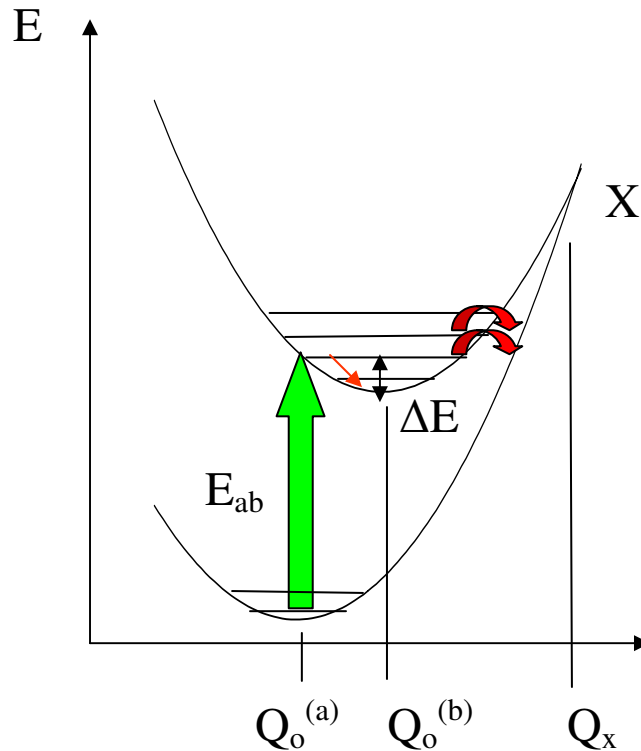


Figure 1. Configuration coordinate model of nonradiative transitions between electronic levels in transition metal ions. Q_0 is the equilibrium position of the configuration coordinate with “a” referring to the ground electronic manifold and “b” referring to the first excited electronic manifold. The horizontal lines are harmonic oscillator vibrational sublevels. The crossover point at Q_x is too high for significant nonradiative transfer but tunneling from “b” to “a” can occur (the curved arrows) leading to nonradiative transfer that increases with temperature.

In general, compounds have phonon energies that decrease as the mass of the anion increases. Thus the phonon energy decreases in the following order: oxide, fluoride, selenide, chloride, iodide, and bromide compounds. [11] If we consider cation-anion pairs as harmonic oscillators with spring constant k and mass m , the frequency ν is

$$\nu \propto \sqrt{k/m} \quad (3)$$

so the higher mass anions would lead to a lower frequency phonon. To achieve efficient room-temperature operation of an infrared transition metal laser, we should therefore look for hosts with small phonon energies for low nonradiative relaxation rates and small crystal fields for appropriate infrared energy level splittings.

3.1 The II-VI breakthrough

In 1995, a group of researchers at Lawrence Livermore National Laboratory reported a new class of room-temperature, widely tunable, mid-IR laser materials. The active ion was Cr^{2+} and the host materials consisted of II-VI semiconductor compounds. [12, 13] This breakthrough discovery initiated a flurry of activity in the development of Cr^{2+} lasers. The initial Livermore report used ZnS and ZnSe as the II-VI host materials. Other researchers, including my group at the Air Force Research Laboratory, showed that other II-VI host materials such as CdSe [14, 15] and even ternary mixtures of $\text{Cd}_x\text{Mn}_{1-x}\text{Te}$ [16] could be used as Cr^{2+} laser host materials. These room temperature laser demonstrations were possible because of the low maximum phonon frequencies observed in II-VI compounds, e.g. 250 cm^{-1} in ZnSe. The Cr^{2+} nonradiative relaxation rate remains small relative to the radiative rate below 300K for many of the II-VI host materials.

3.2 Cr^{2+} spectroscopy

The Cr^{2+} ion has the $3d^4$ electronic configuration. So there are 4 unpaired electrons in the d orbitals or equivalently one hole. The single hole aspect of the Cr^{2+} ion makes its energy level splitting in a crystal field analogous to the splitting observed for the Ti^{3+} ion, a $3d^1$ configuration. One difference lies in the fact that Cr^{2+} ions substitute for II-Group elements in II-VI compounds and thus experience tetrahedral crystal field symmetry while in Ti^{3+} -doped oxides, the Ti^{3+} ion experiences an octahedral crystal field symmetry. The tetrahedral field for identical ion-to-ligand distances changes the sign of the Dq splitting parameter and reduces it in value compared to an octahedral field according to the following formula: [17]

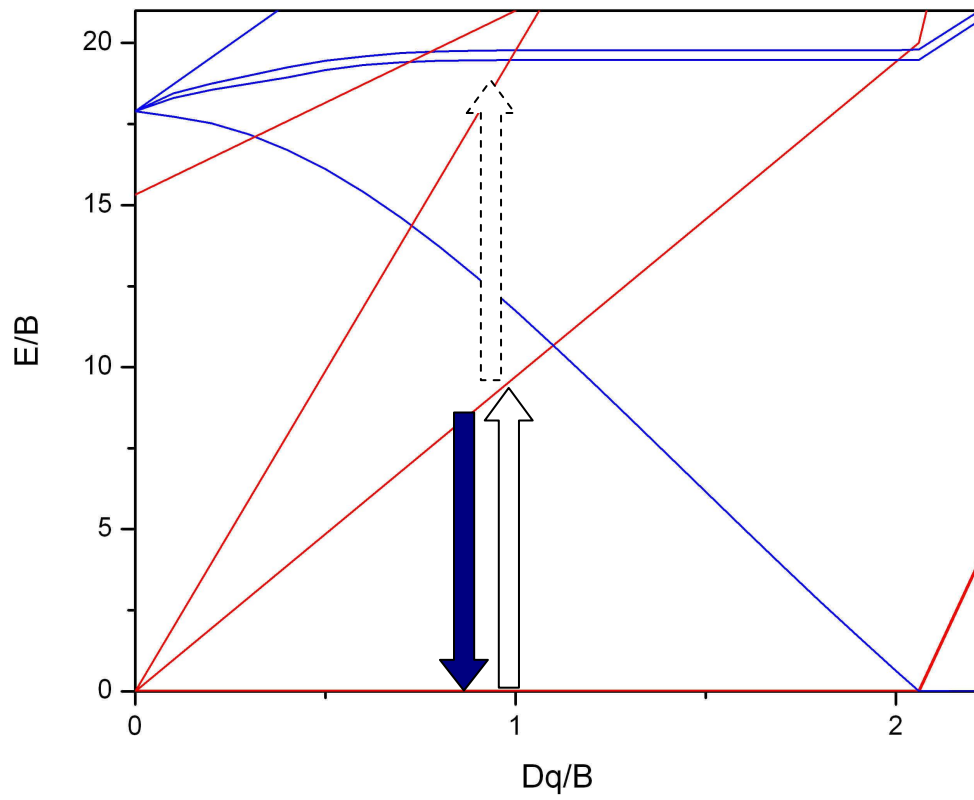
$$Dq(\text{tetrahedral}) = -4/9 Dq(\text{octahedral}) \quad (4)$$

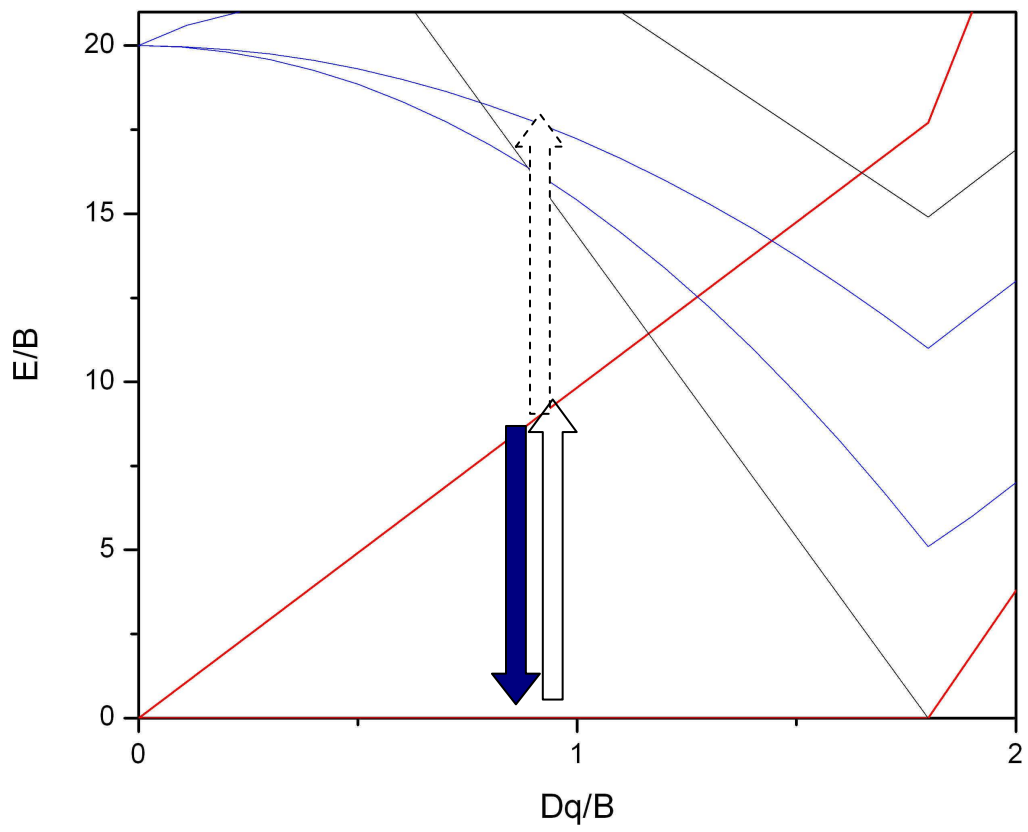
However, consideration of the $3d^4$ configuration of the Cr^{2+} ion as a single hole rather than a single electron negates the sign change. Thus Cr^{2+} has the same level labels as Ti^{3+} (except for total electron spin of 5 vs. 2) and a smaller crystal field splitting. For this reason Cr^{2+} is sometimes known as the infrared titanium sapphire laser.

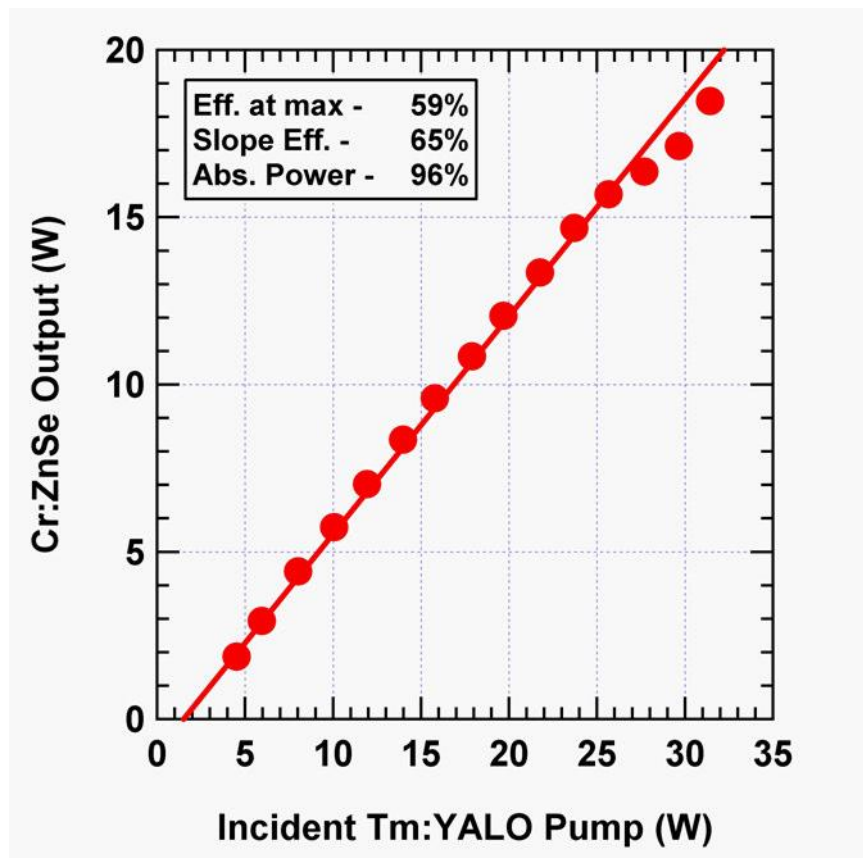
The crystal field splitting and Jahn-Teller splitting of upper and lower degenerate d levels result in broadband absorption in the $1.5\text{-}2.1 \mu\text{m}$ region and broadband emission in the $1.8\text{-}3.1 \mu\text{m}$ region for $\text{Cr}^{2+}:\text{ZnSe}$. Other II-VI hosts show small shifts in these bands due to differences in the crystal field Dq splitting. CdSe has a smaller crystal field with a shift of absorption and emission peaks to longer wavelengths; a $\text{Cr}^{2+}:\text{CdSe}$ laser has been tuned out to $3.4 \mu\text{m}$. [18] $\text{Cr}^{2+}:\text{ZnS}$ has a higher crystal field splitting with a $\sim 100 \text{ nm}$ shift of absorption and emission peaks to shorter wavelengths.

3.3 Why no Cr^{2+} Excited State Absorption?

The tuning limitations of Co^{2+} and Ni^{2+} caused by excited state absorption have already been mentioned. Other transition metal laser ions such as Cr^{3+} in alexandrite [19] and Ti^{3+} in YAlO_3 [20] have excited state absorption (ESA) which limits tuning or prevents lasing altogether. Tanabe-Sugano diagrams [21] show the crystal field splitting of $d^1\text{-}d^9$ electronic configurations. A look at these diagrams is helpful for understanding optical transitions in transition metal ions. Co^{2+} in a site with octahedral symmetry has a 4F free ion state split by the crystal field into a 4T_1 ground state, a 4T_2 first excited state, and a 4A_2 second excited state. Absorption and emission transitions between the 4T_1 ground state and the 4T_2 first excited state are spin allowed. However, as Figure 2 shows, ESA from the 4T_2 first excited state to the 4A_2 second excited state is also spin allowed. Transitions from the 4T_2 first excited state to the 4T_1 state that comes from the 4P free ion level may also contribute to ESA. All other relatively low states are spin multiplicity $2S + 1 = 2$ levels and are spin forbidden.







5. Fe²⁺ TRANSITION METAL LASERS

The Fe²⁺ ion has a 3d⁶ electronic configuration. Five of the electrons compose a half-filled d shell so the d⁶ configuration has similarities to the d¹ configuration. In II-VI hosts it is expected to have spectroscopy similar to Cr²⁺ ions but with opposite sign due to the presence of a single electron rather than a single hole. The ⁵D free ion level is split by a tetrahedral crystal field into a ⁵E ground state level and a ⁵T₂ first excited state. Higher levels come from free ion levels with lower spin multiplicity and thus are expected to not have significant ESA.

However, Fe²⁺ ions in hosts studied to this time have multiphonon nonradiative transition rates that increase rapidly with temperature, quenching the ⁵T₂ first excited state lifetime strongly at room temperature. Thus the first demonstration of Fe²⁺ lasing [32] was done at a temperature of 2K in 1983. Laser oscillation was observed at 3.53 μm in n-InP. The longer absorption and emission wavelengths of Fe²⁺ imply that the crystal field splitting parameter Dq is smaller for Fe²⁺ compared to Cr²⁺. For the same phonon coupling strength, this is likely to lead to the higher nonradiative relaxation rate observed for Fe²⁺.

More recently (1999), use of ZnSe for the Fe²⁺ host enabled laser operation at temperatures up to 180K. [33] The authors achieved temperature tuning of the wavelength between 3.98 μm and 4.54 μm. Room temperature operation was achieved in 2005 [34] by keeping the pump pulse and lasing pulse shorter than the relaxation lifetime, i.e. using gain switched pumping. Unfortunately, the limitation of Fe²⁺ lasers to gain-switched pulses or cryogenic cooling is likely to limit Fe²⁺ to being an interesting but somewhat impractical laser ion for most commercial applications similar to Co²⁺.

6. Cr²⁺ TRANSITION METAL LASER ISSUES

6.1 Cr²⁺:ZnSe thermal lensing

Assuming a uniformly pumped, side-cooled cylinder, and neglecting the impact of strains in the laser rod, thermal lens power TLP (diopters) can be estimated as [12]:

$$TLP = 1/f \approx \frac{P_a}{2\kappa A} \frac{dn}{dT} \quad (5)$$

where f is thermal lens focal length, κ is thermal conductivity, A is laser beam cross sectional area, P_a is the absorbed power in the rod, and dn/dT is the change in refractive index with temperature. Note that the thermal lens power is proportional to the product of absorbed power per unit area (absorbed intensity) and the ratio of dn/dT to κ . The lower the ratio of dn/dT to κ , the more power per unit area can be absorbed for the same thermal lens power. While ZnSe has good thermal conductivity, it has a very large $dn/dT = 70 \times 10^{-6} \text{ K}^{-1}$. This makes power scaling difficult due to the generation of thermal lensing in the material by absorbed pump power not reconverted to optical radiation. Thermal lensing power for a given heat load will be 9x stronger in ZnSe than in sapphire, and 4.3x stronger than in YAG. Thermal lensing in CdSe will be 19x stronger even than in ZnSe. Thermal management is therefore expected to be a significant issue in designing lasers based upon II-VI materials.

Power scaling Cr²⁺ laser output to multi-watt levels requires a geometry designed for maximum suppression of thermal effects. An attractive approach is the face-cooled disk design, [23] essentially a gain medium which is both pumped and cooled longitudinally through its large polished faces. Use of a pump spot larger in diameter than the disk thickness ensures that the pump-induced heat is primarily extracted longitudinally, reducing the radial thermal gradients responsible for thermal lensing in the active medium. Such a strategy has contributed to outputs in the hundreds of watts from Nd:YAG systems. [35] Although the thermal lensing effect is stronger in ZnSe, the technique has promise for Cr²⁺ lasers as well.

Both severe thermal lensing and strong disk heating were observed in an interferometric characterization of Cr²⁺:ZnSe disks pumped by a 0.4-mm radius, multi-mode, 2.05-μm laser beam. [36] Thermal lensing as strong as 2.3 diopters per watt of pump power was measured in a 1-mm disk, and longitudinally averaged temperature increases of up to 10 °C per watt of pump power were calculated from a finite element model (see Figure 5). Disk heating to the point of increased Cr²⁺ nonradiative relaxation is possible with only a few watts of pump power indicating that absolute material temperature and thermal gradients must be controlled to achieve high efficiency and high power.

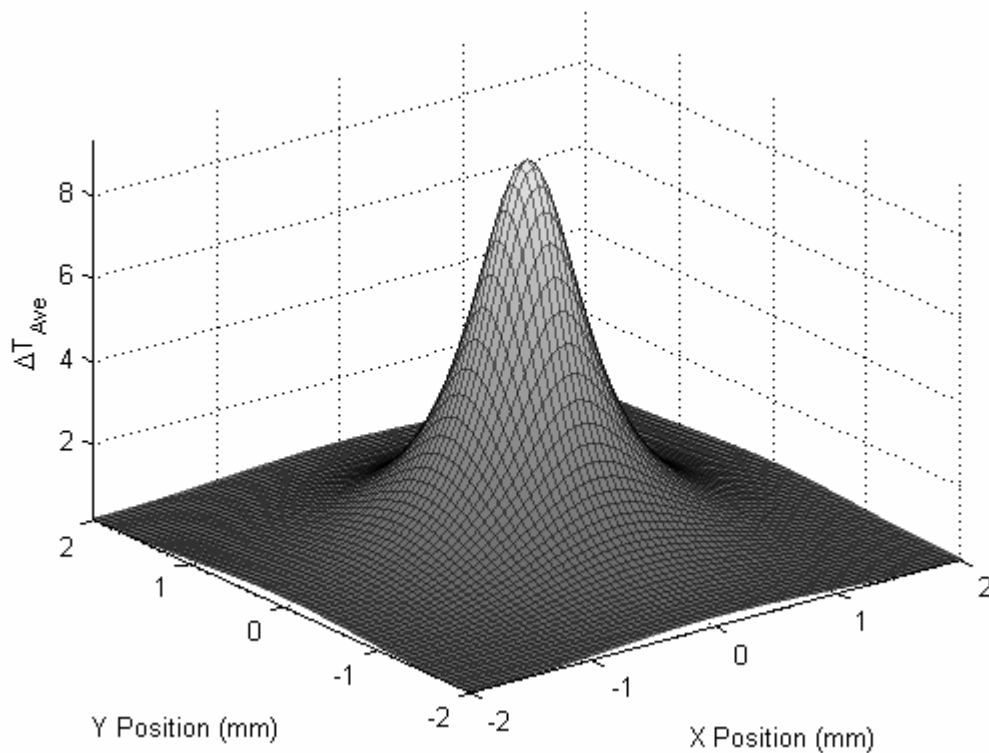


Figure 5. Longitudinally [along the disk thickness] averaged temperature distribution in a 1-mm thick Cr²⁺:ZnSe disk predicted for 1-W heat load with a 0.4-mm radius Gaussian beam.

Various geometries designed to reduce absolute temperature and thermal gradients have been considered. Using ZnSe windows as heat sinks on both sides of a Cr²⁺:ZnSe thin disk to achieve cooling from both sides appeared promising. However, laser performance was disappointing primarily due to the difficulty in achieving good optical contact between the window and laser disk. Improved polishing techniques are needed to produce highly flat surfaces.

6.2 Cr²⁺:ZnSe concentration quenching

The quenching of radiative lifetime with increasing concentration above ~100 ppm substitution for the Zn²⁺ ion is well known. But the reason for this is not well understood. In other solid-state laser materials, like Nd:YAG, concentration quenching does not take effect until concentrations reach several percent. At this concentration, nearest neighbor pairs of Nd³⁺ are likely to occur assuming random substitution at the Y³⁺ sites. The Nd³⁺ neighbor pairs act as sinks for the excitation energy which can hop from ion to ion until fluorescence occurs or a Nd³⁺-Nd³⁺ pair is found. But Cr²⁺ ions exhibit quenching at concentration levels at least two orders of magnitude smaller. This may indicate that Cr²⁺ ions are not randomly distributed but are concentrated at certain locations in the laser material. One possibility is that the Cr²⁺ ions preferentially diffuse into polycrystalline material along grain boundaries. Typical grain sizes of polycrystalline ZnSe are 70 μm. A boundary layer 1 μm thick would compose 0.9% of the sample volume thus explaining the two order of magnitude discrepancy. A volume scan for emission intensity with 1-μm³ resolution could confirm or refute this hypothesis. Polycrystalline material with smaller grain size should also be investigated; a 10-μm grain would have 60% of its volume in a 1-μm thick boundary allowing a potential 60x increase in Cr²⁺ concentration based on this hypothesis.

6.3 Direct electrical pumping of $\text{Cr}^{2+}:\text{ZnSe}$

It has been known for decades that wide-band-gap II-VI semiconductors (pure and doped with acceptors and donors) are electroluminescent. It was also noticed that the presence of transition metal ions as inadvertent dopants effectively quenched the visible light emission from donor-acceptor pairs. In 1974 Grebe and Schultz reported the details of Cr^{2+} absorption and emission in ZnS and interpreted quenching as Cr^{2+} capture of conduction band free carriers. [37] Indirect optical excitation of Fe^{2+} lasing via free carriers in InP was demonstrated in 1984 [32] indicating that Cr^{2+} lasing via indirect optical pumping of the bandgap and perhaps even electrical pumping of Cr^{2+} lasing may be possible. Recently, Mirov's group demonstrated room temperature direct electroluminescence of Cr^{2+} in n-ZnSe at 2-3 μm , 8 μm and visible 0.600 μm wavelengths. [38] They expect use of p-n junction structures should lead to increased efficiency of energy transfer and a possible lasing demonstration.

6.4 A fiber $\text{Cr}^{2+}:\text{II-VI}$ laser?

The strong thermal lensing of Cr^{2+} -doped II-VI materials is a major issue when designing Cr^{2+} lasers and especially when scaling power. The thin disk design exchanges the benefit of reduced thermal lensing for the added complexity of multi-pass pumping to assure that the pump power is efficiently absorbed. It does not solve the problem of overall temperature rise that gets worse as the disk thickness gets smaller and leads to higher nonradiative relaxation rates.

An interesting possibility would be a fiber format. A fiber with the proper core radius and core/cladding refractive indices can confine beam propagation in a way that is insensitive to radial temperature gradients. In addition, doping can be low as required to prevent concentration quenching. But pump power can be efficiently absorbed by making the fiber long enough to efficiently absorb the pump power. The only limit to concentration would be the requirement that gain per unit length would need to be greater than passive loss per unit length.

Unfortunately, expertise in silica fiber pulling does not translate easily to making fiber cores from polycrystalline II-VI materials. Chalcogenide glass has been fabricated and shown to incorporate rare earth ions. [39] However, incorporation of chromium in the proper oxidation state (Cr^{2+}) with the proper tetrahedral site symmetry has not been achieved in any infrared glass to my knowledge. Promising ideas to fabricate Cr^{2+} -doped II-VI fibers have not yet been found.

7. CONCLUSIONS

The history of transition metal lasers is as long as the history of lasers themselves but great progress has been made in their development for practical applications since the advent of the Cr^{2+} laser. The 1995 innovation of pairing Cr^{2+} with a II-VI semiconductor host that has tetrahedral symmetry substitution sites has led to demonstration of broadly tunable, room temperature, mid-IR lasers. Cr^{2+} lasers have achieved output power of 18 W, tuning range of 1100 nm, and modelocked operation down to 100 fsec.

Thermal lensing, thermally induced emission quenching, and concentration quenching are issues that challenge further power scaling. Concepts to address these issues are under development. New ideas such as direct electrical pumping and fabrication of a Cr^{2+} fiber laser are currently being tested. Use of Cr^{2+} lasers in future applications looks promising.

ACKNOWLEDGEMENTS

Financial support by the Air Force Office of Scientific Research and the Sensors Directorate of the Air Force Research Laboratory are gratefully acknowledged. Years of intensive effort to investigate and develop Cr^{2+} laser devices by graduated students Jason McKay and Debra Krause as well as present student Patrick Berry are also acknowledged and sincerely appreciated.

REFERENCES

1. Maiman, T.H., *Stimulated optical radiation in ruby*. Nature, 1960. **187**: p. 493-494.
2. Walling, J.C., et al., *Tunable-laser performance in $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$* . Optics Letters, 1979. **4**: p. 182-183.

3. Johnson, L.F., R.E. Dietz, and H.J. Guggenheim, *Optical maser oscillation from Ni^{2+} in MgF_2 involving simultaneous emission of phonons*. Physical Review Letters, 1963. **11**: p. 318-320.
4. Johnson, L.F., R.E. Dietz, and H.J. Guggenheim, *Spontaneous and stimulated emission from Co^{2+} ions in MgF_2 and ZnF_2* . Applied Physics Letters, 1964. **5**: p. 21-22.
5. Moulton, P.F., A. Mooradian, and T.B. Reed, *Efficient cw optically pumped $Ni:MgF_2$* , Optics Letters, 1978. **3**: p. 164-168.
6. Iverson, M.V. and W.A. Sibley, *Temperature dependence of Ni^{2+} luminescence in $KZnF_3$, MgF_2 and MgO* , Journal of Luminescence, 1979. **20**: p. 311.
7. Moulton, P.F., *An investigation of the $Co:MgF_2$ laser system*, IEEE Journal of Quantum Electronics, 1985. **21**: p. 1582-1595.
8. Fox, A.M., A.C. Maciel, and J.F. Ryan, *Efficient cw performance of a $Co:MgF_2$ laser operating at 1.5-2.0 μm* , Optics Communication, 1986. **59**: p. 142-144.
9. DiLieto, A., *Development of a cw $Co:MgF_2$ laser*, Optics and Lasers in Engineering, 2003. **39**: p. 305-308.
10. Welford, D. and P.F. Moulton, *Room-temperature operation of a $Co:MgF_2$ laser*, Optics Letters, 1988. **13**: p. 975.
11. Sorokina, I.T., *Crystalline Lasers*, in *Solid-State Mid-Infrared Laser Sources*, I.T. Sorokina and K.L. Vodopyanov, Editors. 2003, Springer: Berlin.
12. Page, R.H., et al. *Cr^{2+} -doped II-VI crystals: new widely tunable, room-temperature mid-IR lasers*, in *Lasers and Electro-Optics Society Annual Meeting*. 1995: IEEE.
13. DeLoach, L.D., et al., *Transition metal-doped zinc chalcogenides: spectroscopy and laser demonstration of a new class of gain media*, IEEE Journal of Quantum Electronics, 1996. **32**(6): p. 885-895.
14. Schepler, K.L., S. Kück, and L. Shiozawa, *Cr^{2+} emission spectroscopy in $CdSe$* . Journal of Luminescence, 1997. **72-74**: p. 116-117.
15. McKay, J., K.L. Schepler, and G.C. Catella, *Efficient grating tuned mid-IR $Cr^{2+}:CdSe$ laser*, Optics Letters, 1999. **24**(22): p. 1575-1577.
16. Hömmerich, U., et al., *Demonstration of room-temperature laser action at 2.5 μm from $Cr^{2+}:Cd_{0.85}Mn_{0.15}Te$* . Optics Letters., 1997. **22**(15): p. 1180-1182.
17. Henderson, B. and G.F. Imbusch, *Optical spectroscopy of inorganic solids*, 1989, New York: Oxford University Press. 645.
18. McKay, J., W. Roh, and K.L. Schepler, *Extended mid-IR tuning of a $Cr^{2+}:CdSe$ laser*. in *Advanced Solid-State Lasers*. 2002: Optical Society of America, Washington, DC.
19. Shand, M.L., J.C. Walling, and R.C. Morris, *Excited-state absorption in the pump region of alexandrite*, Journal of Applied Physics, 1981. **52**(2): p. 953-955.
20. Petermann, K. and T. Wegner, *Excited state absorption of $Ti^{3+}:YAlO_3$* , Applied Physics B, 1989. **B49**(3): p. 275-278.
21. Tanabe, Y. and S. Sugano, *On the absorption spectra of complex ions*, Journal of the Physics Society of Japan, 1954. **9**: p. 753-779.
22. McKay, J. and K.L. Schepler, *Cr^{2+} Lasers: Efficient, broadly tunable Mid-IR laser sources in Solid-state and diode laser technology review*. 2001. Albuquerque NM: Directed Energy Professional Society.
23. McKay, J.B., W.B. Roh, and K.L. Schepler, *4.2 W $Cr^{2+}:ZnSe$ face cooled disk laser* in Technical Digest Summaries of papers presented at the Conference on Lasers and Electro-Optics. Conference Edition, 19-24 May 2002. Long Beach, CA, USA: Optical Society of America.
24. Carrig, T.J., et al. *Chromium-doped chalcogenide lasers* in *Solid State Lasers and Amplifiers*, 27-29 April 2004 *Proceedings of the SPIE - The International Society for Optical Engineering*. 2004. Strasbourg, France: SPIE-Int. Soc. Opt. Eng.
25. Wagner, G.J. and T.J. Carrig, *Power scaling of $Cr^{2+}:ZnSe$ lasers* in *Advanced Solid-State Lasers*. 2001: Optical Society of America, Washington DC.
26. Page, R.H., et al., *Cr^{2+} -doped zinc chalcogenides as efficient, widely tunable mid-infrared lasers*, IEEE Journal of Quantum Electronics, 1997. **33**: p. 609-619.
27. Sorokina, I.T., et al., *Efficient broadly tunable continuous-wave $Cr^{2+}:ZnSe$ laser*, Journal of the Optical Society of America B, 2001. **18**: p. 926-930.
28. Wagner, G.J., et al. *Single-frequency $Cr:ZnSe$ laser*. in *Advanced Solid-State Photonics, Proceedings Volume, Feb 1-4 2004*. 2004. Santa Fe, NM, Optical Society of America, Washington, DC.
29. Carrig, T.J., et al., *Mode-locked $Cr^{2+}:ZnSe$ laser*, Optics Letters, 2000. **25**: p. 168-170.

30. Sorokina, I.T., et al. *Active and passive modelocking of the Cr²⁺:ZnSe laser* in *Advanced Solid-State Lasers*. 2001. Optical Society of America, Washington DC.
31. Sorokina, I.T., E. Sorokin, and T.J. Carrig. *Femtosecond pulse generation from a SESAM mode-locked Cr:ZnSe laser*, in *Conference on Lasers and Electro-Optics*. 2006. Long Beach CA: Optical Society of America, Washington DC.
32. Klein, P.B., J.E. Furneaux, and R.L. Henry, *Laser oscillation at 3.53 μm from Fe²⁺ in n-InP:Fe*. Applied Physics Letters, 1983. **42**: p. 638.
33. Adams, J.J., et al., *4.0–4.5- μm lasing of Fe:ZnSe below 180 K, a new mid-infrared laser material*. Optics Letters, 1999. **24**: p. 1720-1722.
34. Kernal, J., et al., *3.9-4.8 μm gain-switched lasing of Fe:ZnSe at room temperature*. Optics Express, 2005. **13**(26): p. 10608-10615.
35. Contag, K., et al. *Power scalability and beam quality of the thin disk laser*. in *Conference on Lasers and Electro-Optics*. 2000: Optical Society of America, Washington DC.
36. Schepler, K.L., et al., *Thermal effects in Cr²⁺:ZnSe thin disk lasers* IEEE Journal of Selected Topics in Quantum Electronics, 2005. **11**(3): p. 713-720.
37. Grebe, G. and H.-J. Schultz, *Luminescence of Cr²⁺ centres and related optical interactions involving crystal field levels of chromium ions in zinc sulfide*, Zeitschrift Naturforschung A, 1974. **29**: p. 1803-1819.
38. Luke, L., et al., *Middle-infrared electroluminescence of n-type Cr doped ZnSe crystals*. in *Solid-State Lasers XV: Technology and Devices*. 2006. San Jose CA: Proc. of SPIE.
39. Aggarwal, I.D., L.B. Shaw, and J.S. Sanghera, *Chalcogenide Glass for Mid- and Long-Wave IR Fiber Lasers* in *Fiber Lasers II: Technology, Systems, and Applications*. 2005. San Jose: SPIE, Bellingham, WA.